Water Sorption Mechanisms for MIS Materials

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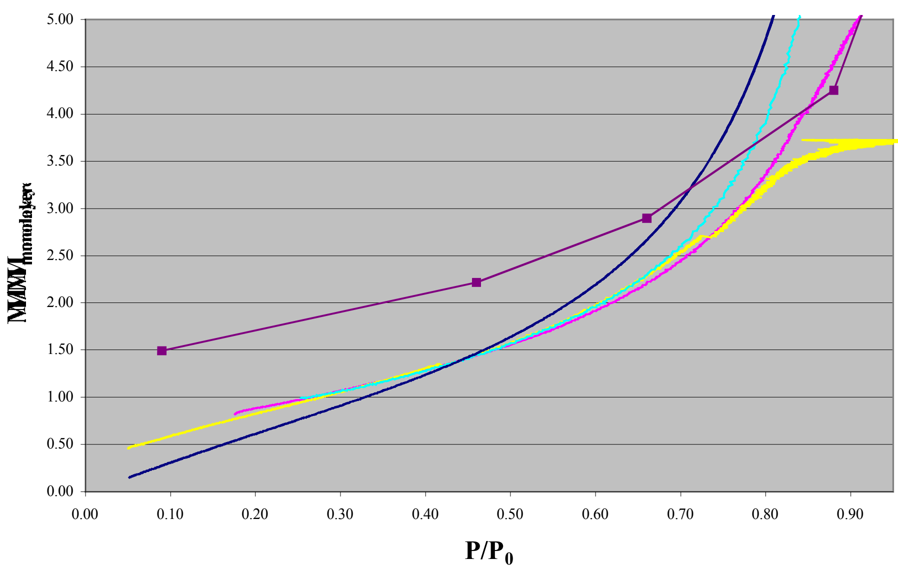
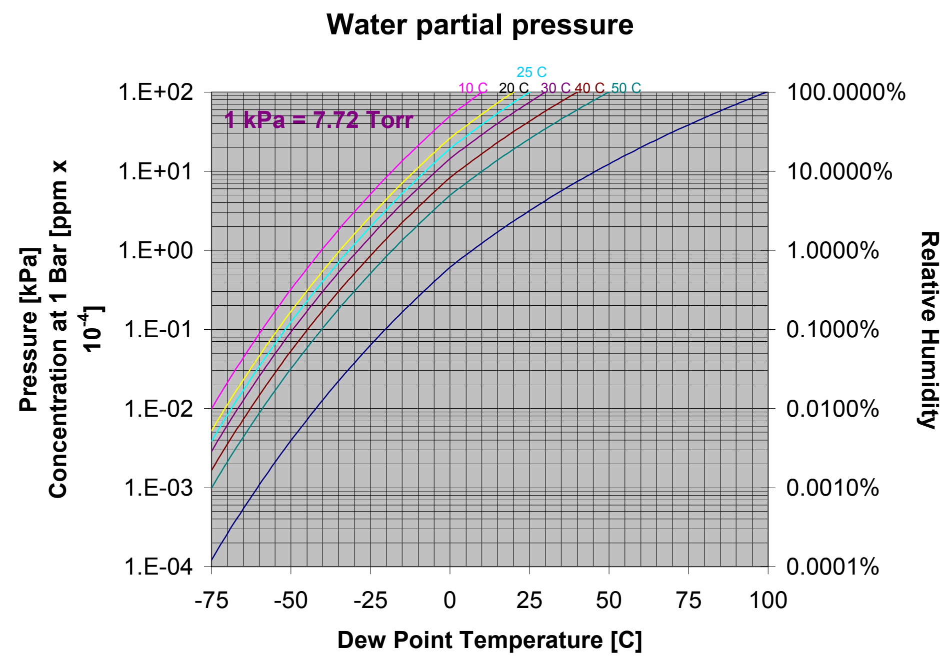




$$\Delta G^0 = \left[\Delta H^0_{298} + \Delta H_{ads} - T \cdot \Delta\Phi^0\right]$$

Requirements of DOE's 3013 Standard

DOE-STD-3013-2000 "Stabilization, Packaging, and Storage Standard for Plutonium-bearing Materials" addresses the requirements for safe long-term storage of 34 metric tons of excess weapons plutonium.

- >30wt% plutonium (impurities can include processing salts NaCl, KCl, $CaCl_2$, $MgCl_2$).
- Oxide material must be stabilized at 950 °C for 2 hours. Stabilization is designed to remove reactive materials, remove water, oxidize organics.
- Packaging to include two welded containers.
- Packaged material must be less than 0.5wt% moisture. Designed to address the potential for H_2 generation due to radiolysis of water.

Defining and Detecting Moisture

- Moisture is any hydrogenous chemical/material that can produce water.
    - Adsorbed water – 18 g/mole.
    - Hydroxyl layer on oxides - 9 g/mole of OH.
    - Waters of hydration ($CaCl_2*6H_2O$) 18 g/mole of H_2O.
    - Hydrides (PuH4) 18 g/$_2$ moles of H.
    - ….

- Loss-on-ignition to 950 °C: All weight loss attributed to "moisture". Problem arises with salts that evaporate, other adsorbed gases such as CO_2, decomposition of sulfates and nitrates, etc.

- At 0.5 wt%, accurate moisture measurement is non-trivial. Proposed techniques are TGA-FTIR, TGA-MS, super critical fluid extraction, neutron moderation, and others may arise.

Adsorption after Stabilization
(assuming stabilization removes all moisture)

•Time between calcination and packaging typcally 24 to 48 hours.

•Moisture in glove boxes range from 60% RH (~20,000 ppm_v), 1000 ppm_v (~3% RH), and 300 ppm_v (~1% RH).

•Consider three classes of materials, which represent most of the material destined for long-term storage:

- −Metal oxides including PuO_2.
- −Deliquescent salts.
- −Hydrated salts.

A Short Discussion on Nomenclature

Dew point temperature (DPT): The temperature at which water vapor is in equilibrium with condensed water or ice, i.e. the saturation water vapor pressure. Best obtained from NIST/ASME Steam Properties Database 1996 (computer program available from NIST). Independent of the temperature or pressure of the gas.

Relative humidity (% RH): The percentage of water vapor saturation of the gas at a given temperature. The ratio of the water vapor pressure to the water vapor pressure at saturation at the temperature of the gas. Related to the chemical activity of the water vapor.

PPM_V: Part per million by volume. The ratio of the partial pressure of the water vapor divided by the total pressure of the atmosphere (with or without the water) multiplied by 10^6. Some instruments assume 760 T.

PPM_W: Part per million by weight. The ratio of the mass of the water vapor in the atmosphere to the mass of the atmosphere. Depends on gas composition.

Moisture uptake by PuO_2

Moisture uptake by PuO_2 powders depends upon:

relative humidity

specific surface area

Specific surface area

- Plutonium dioxide SSA can vary from 50 to 0.1 m^2/g.
- 1 monolayer of water [0.22 mg/m^2] represents 1.1wt% to 0.002%.
- 0.5wt.% of water can vary from 0.5 to 250 monolayers.
- Typical calcined plutonium oxide has an SSA between 5 and .5 m^2/g or 5 to 50 monolayers.

Relative Humidity

PuO_2 powders can adsorb over 0.5 wt% at relative humidities of less 70%.

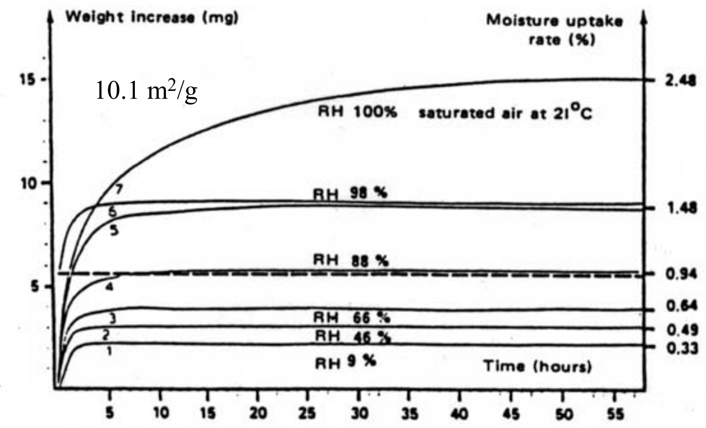


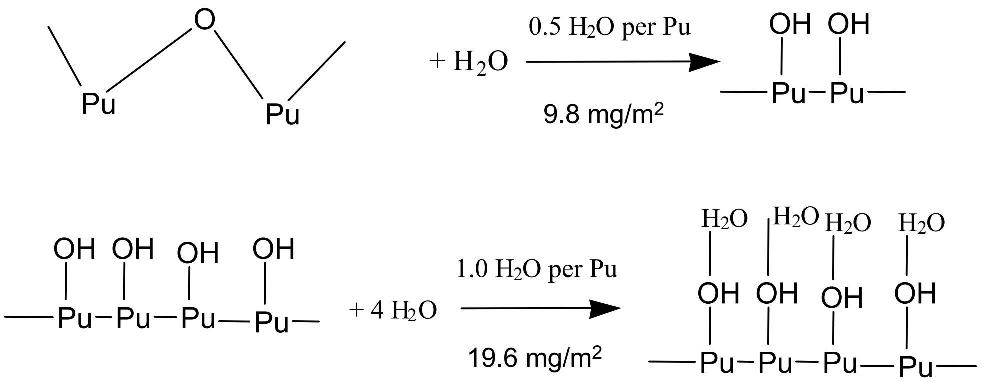
Figure 3. Moisture uptake by PuO_2 powder dried at 600°C.

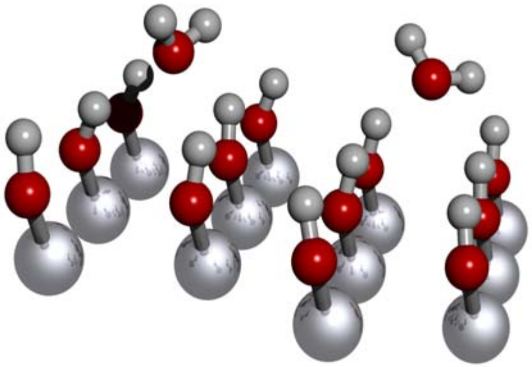
A. Bohhamou and J. P. Beraud, Analusis **8**, 376 (1980)

Water Adsorption from a Crystallographic Point of View

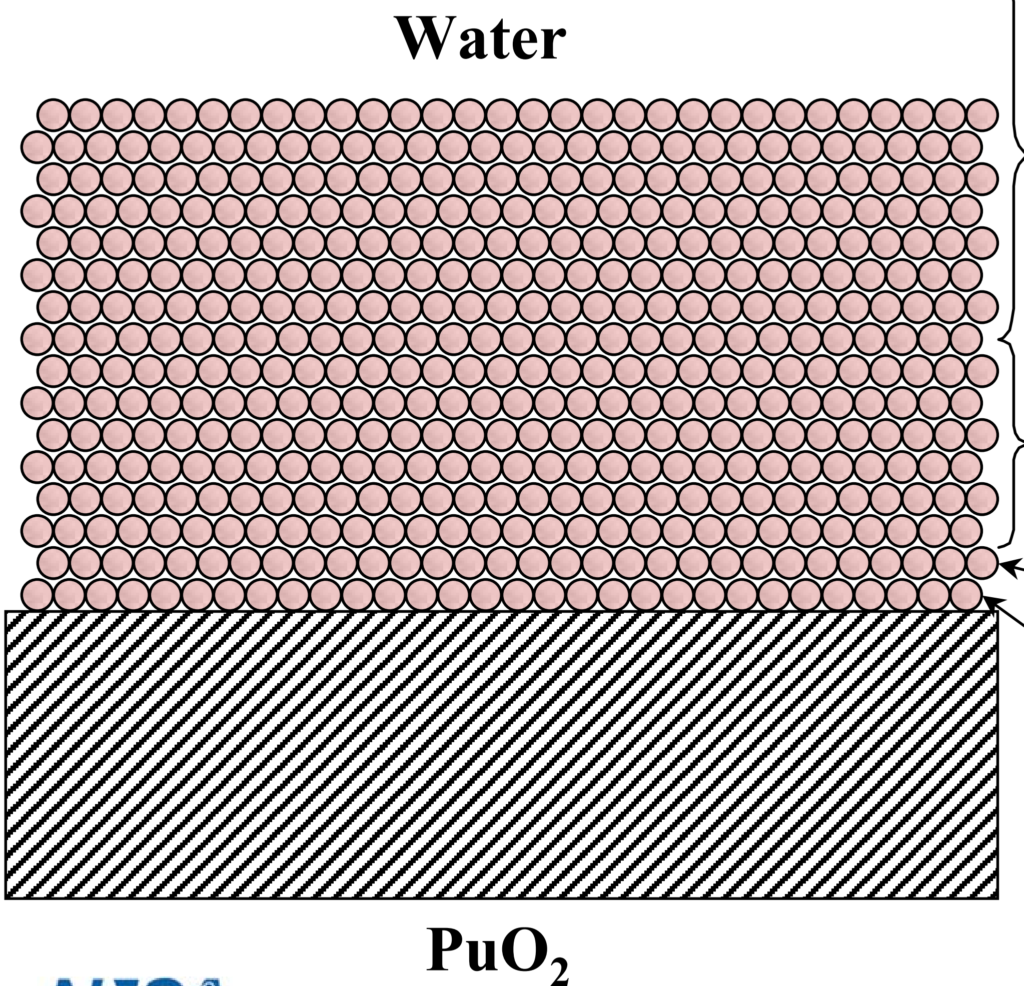
PuO_2 can be described by three dominant faces (100,110,111)

	100 face	110 face	111 face
Pu Atom Density (atom/Å^2)	0.0687	0.0486	.0793
Sorbed Water (mg/m^2)	0.205	0.145	0.237
Stakebake (average mg/m^2)		0.24	
Haschke (mg/m^2)		0.22	
Water (mg/m^2)		0.28	





PuO_2/water model



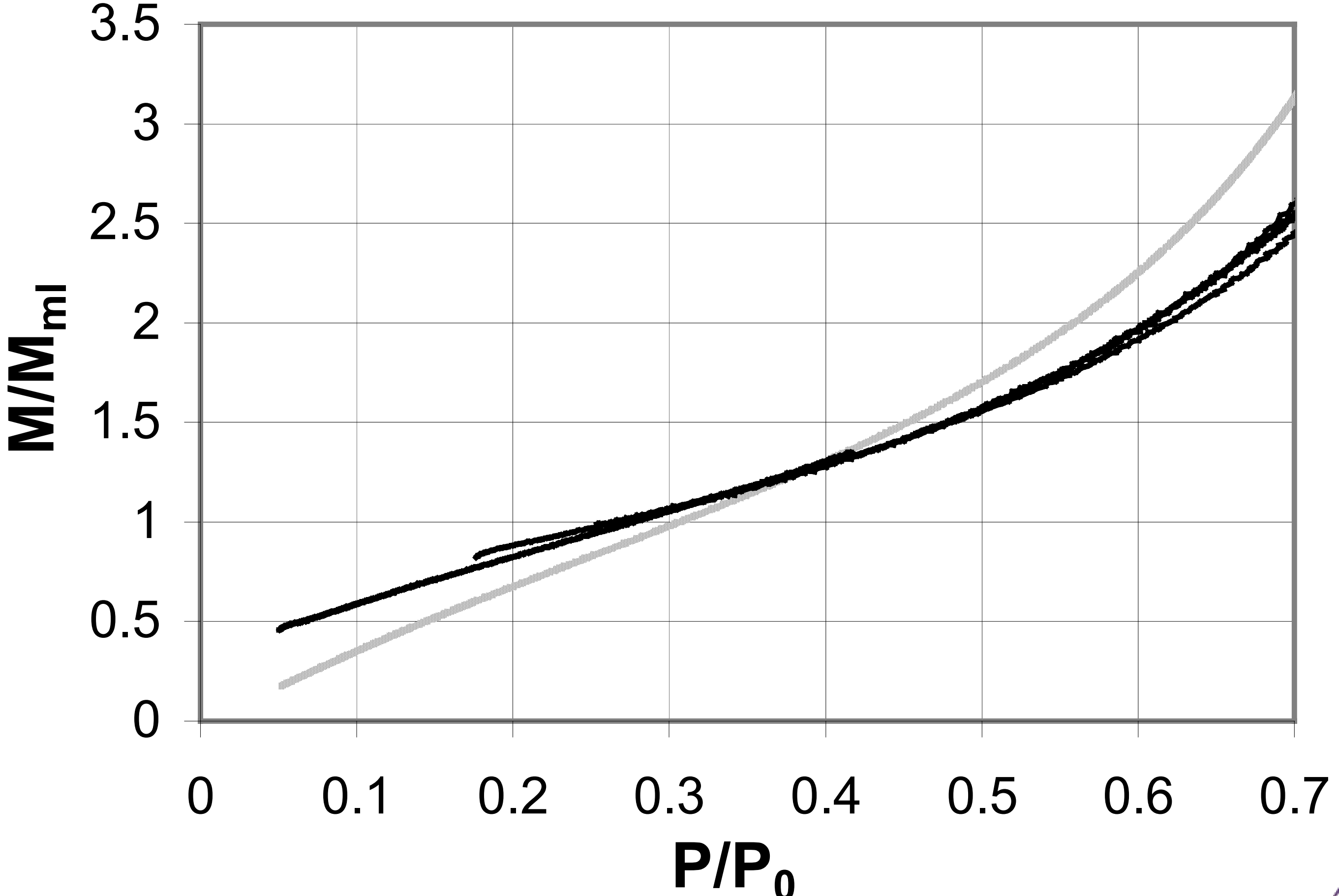
All other layers ΔH_{vap} = 44 kJ/mol the heat of vaporization of water.

Layers 3-8 ΔH_{ads} = 51 kJ/mol Haschke 1997 distinguishes up to 6 layers; ΔH_{ads} estimated from this work.

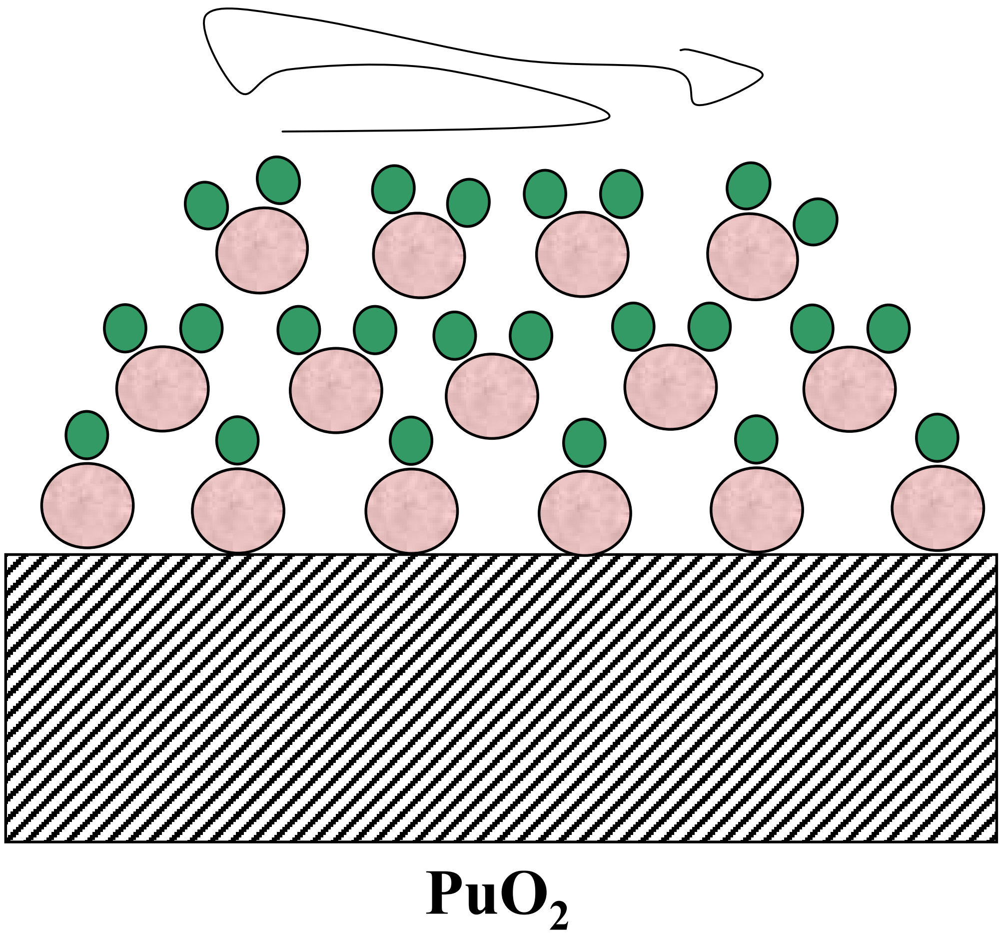
2nd layer ΔH_{ads} = 84 kJ/mol Stakebake 1973

1st layer ΔH_{ads} = 172 kJ/mol Stakebake 1973/Paffett 1999

Moisture adsorption isotherm for PuO_2 powder.



Current PuO_2/water model



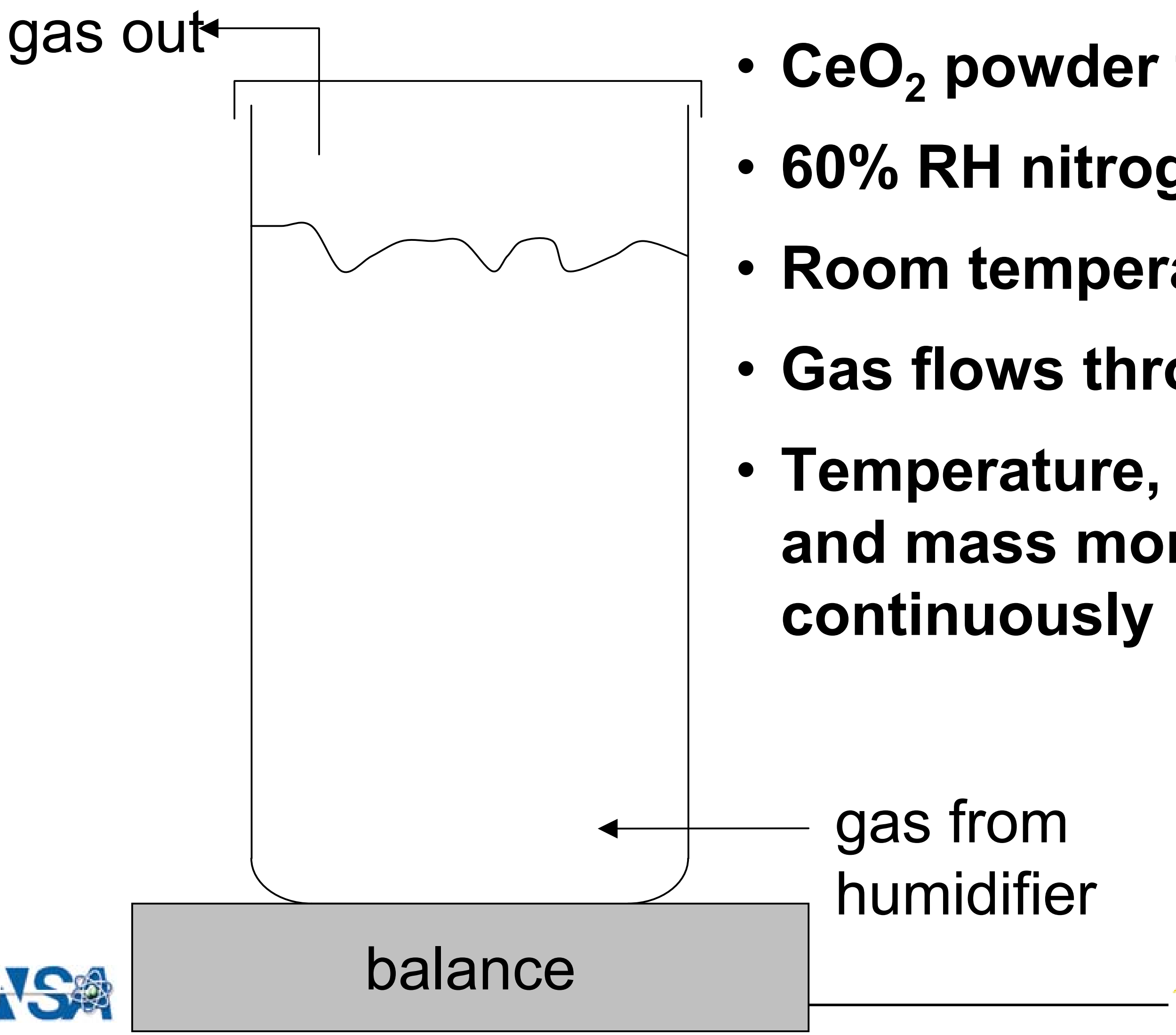
Multilayers of water
$\Delta H \approx 44$ kJ/mol

Layer 3: Second molecularly adsorbed monolayer
$\Delta H \approx 44$ kJ/mol or 47 kJ/mol

Layer 2: First molecularly adsorbed monolayer
$\Delta H \approx 47$ kJ/mol or 80 kJ/mol

Layer 1: Hydroxyl layer equivalent to 1/2 monolayer
$\Delta H \approx 170$ kJ/mol

Verification Cold Tests
Test of mass gain using humidifier



- **CeO_2 powder fills can**
- **60% RH nitrogen gas**
- **Room temperature**
- **Gas flows through powder**
- **Temperature, humidity, and mass monitored continuously**

CeO_2 humidification tests indicate 3 rates for water uptake

•CeO_2 was dried at 400°C for 3 hours - mass loss of 13.1 g

•After humidification tests
(6 SCFH N_2 at 60% RH for 22.8 hours) - mass gain of 13 g

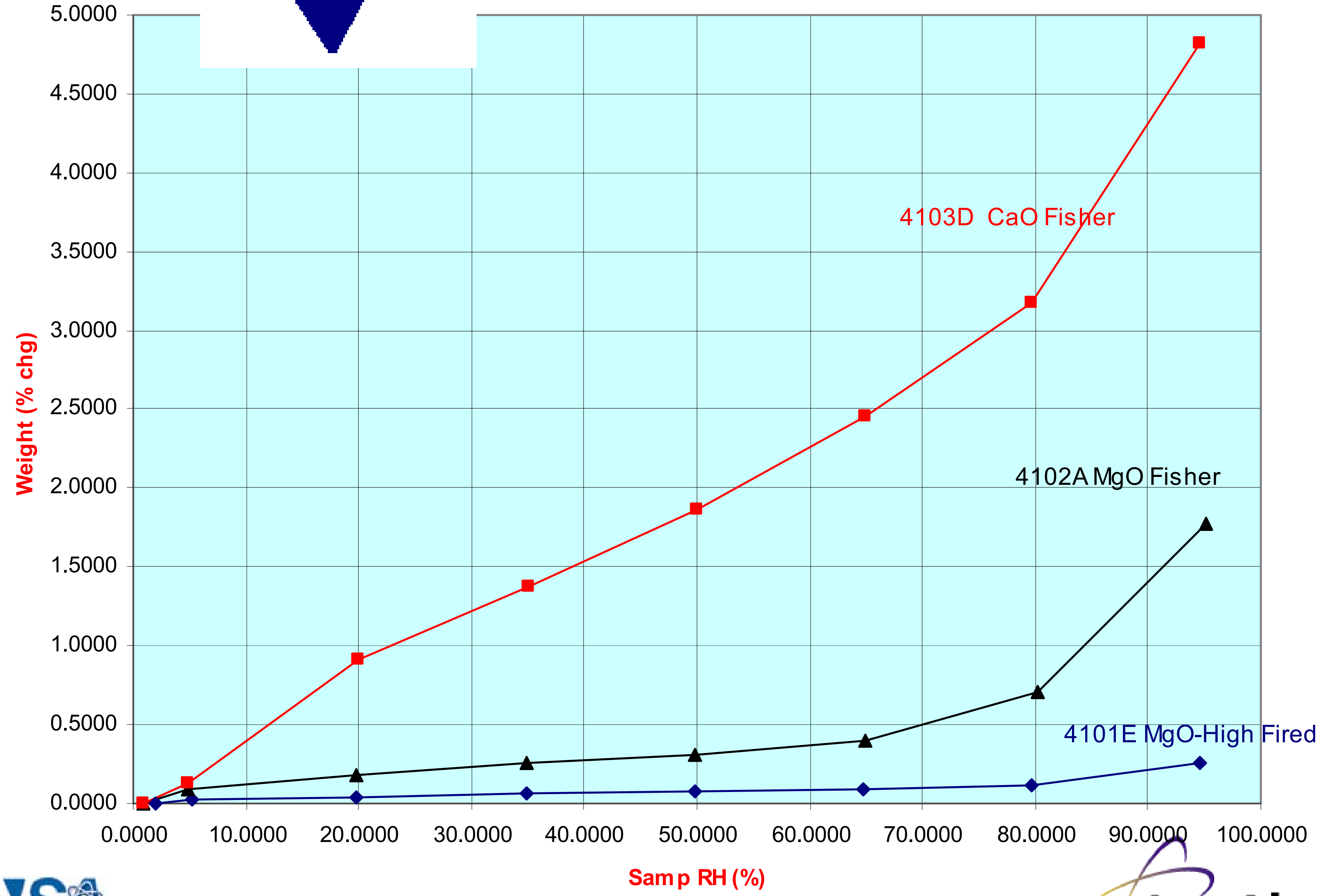
•From mass gain, 4.7 monolayer equivalents of water were adsorbed.

Monolayer equivalents adsorbed		
Mass of CeO_2	3300	g
SSA of CeO_2	3.84	m^2/g
Total surface area	12672	m^2
Mass of water in one monolayer (using 0.22 mg/m^2)	2.8	g
Monolayer equivalents adsorbed	4.7	monolayers

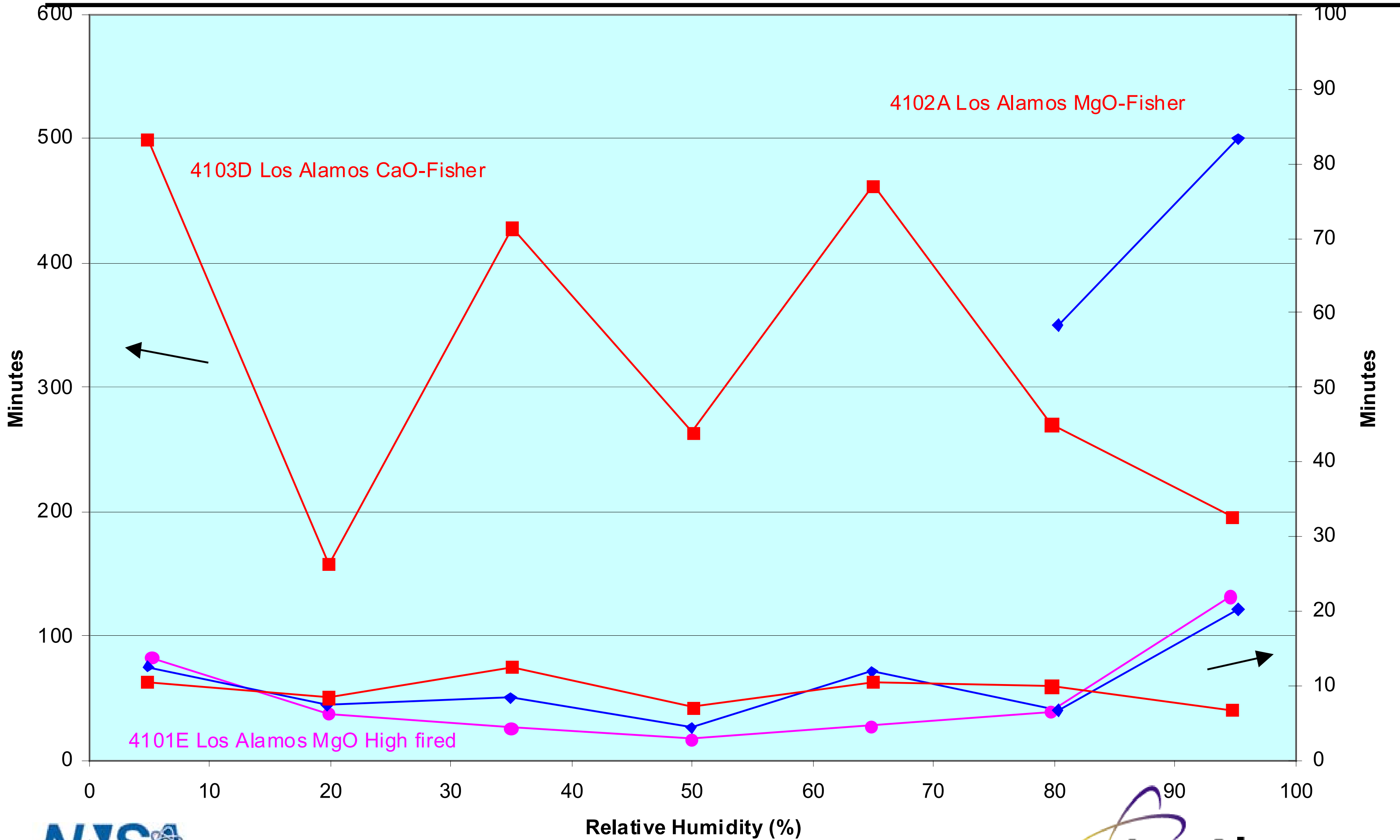
•Rates of mass gain observed under experimental conditions

Rate 1	1.76 g H_2O / hour	
Rate 2	1.17 g H_2O / hour	(66% of 1)
Ending Rate	0.35 g H_2O / hour	(20% of 1)

Isotherm Comparisons



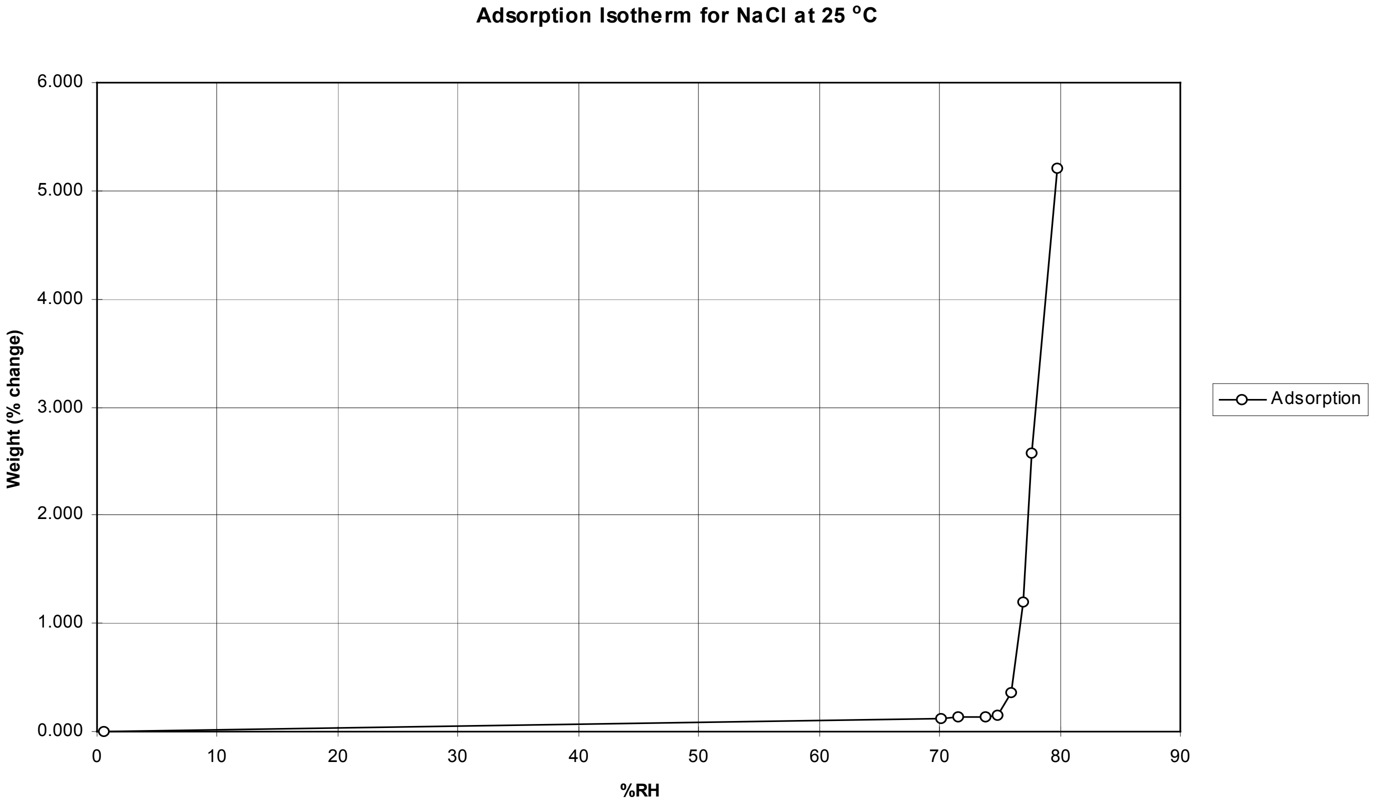
Time constants for moisture sorption



Deliquescent Salts

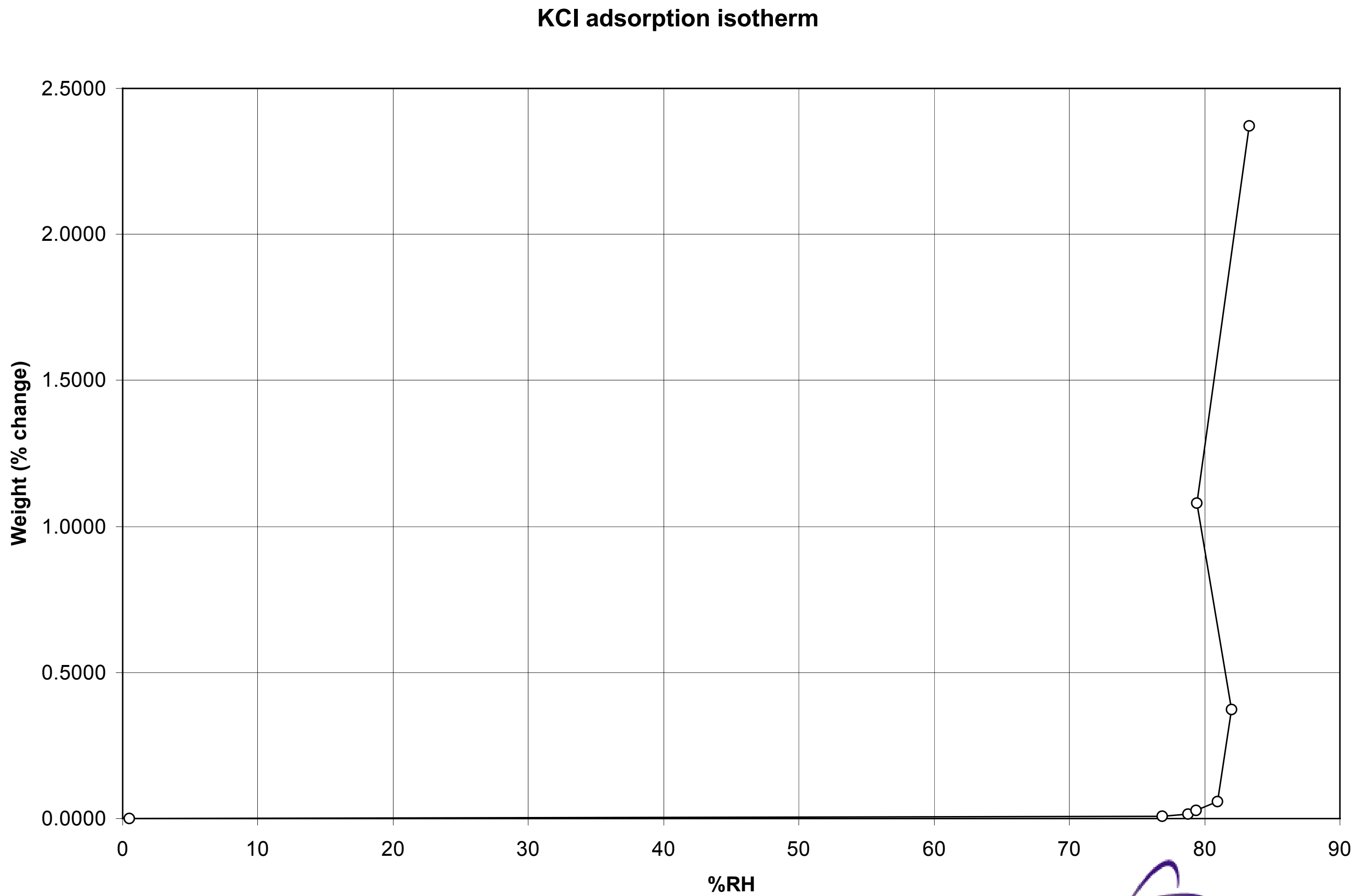
- Typically low specific surface area (melt at stabilization temperatures)
- Typical adsorption isotherm up to deliquescent relative humidity.
- Adsorbs large amounts of water quickly at and above deliquescent relative humidity.

Moisture adsorption isotherm for a typical deliquescent salt



Typical adsorption isotherm for sodium chloride, which deliquesces at 75.3% RH at 25 °C to become a saturated salt solution. (from VTI Corporation, Technical Note #2, Calibration Protocol).

KCl



KCl adsorption isotherm
Weight (% change)
2.5000
2.0000
1.5000
1.0000
0.5000
0.0000
0
10
20
30
40
50
60
70
80
90
%RH

Deliquescent points for common salts.

Table 1: Critical relative humidities of inorganic compounds at 25°. Critical RH is the relative humidity of the saturated solution, i.e. above this relative humidity the compound will pick up moisture until all of the salt is dissolved. "CRC Handbook of Chemistry and Physics 77th Ed.", Ed. D. R. Lide, 1996, CRC Press Boca Raton, Pg. 15-25, and "Moisture Sorption: Practical Aspects of Isotherm Measurement and Use, 2nd Ed." L. N. Bell and T. P. Labuza, American Association of Cereal Chemists, Inc. St. Paul, pgs 33-37.

Compound	Critical RH	Compound	Critical RH	Compound	Critical RH
$CaSO_4$	0.1%	$MgCl_2 \cdot 6H_2O$	33%	NaCl	75%
CsF	3.4%	$NaI \cdot 2H_2O$	38%	NH_4Cl	79%
$LiBr \cdot 2H_2O$	6.4%	K_2CO_3	43%	KBr	81%
$NaOH \cdot H_2O$	6%	$Ca(NO_3)_2 \cdot 4H_2O$	51%	$(NH_4)_2SO_4$	81%
$ZnBr_2 \cdot 2H_2O$	8%	$Mg(NO_3)_2 \cdot 6H_2O$	53%	KCl	84%
$KOH \cdot 2H_2O$	9%	$NaBr \cdot 2H_2O$	58%	$Sr(NO_3)_2 \cdot 4H_2O$	85%
$LiCl \cdot H_2O$	11%	NH_4NO_3	62%	$BaCl_2 \cdot 2H_2O$	90%
$CaBr_2 \cdot 6H_2O$	16%	$CoCl_2$	65%	CsI	91%
$LiI \cdot 3H_2O$	18%	KI	69%	KNO_3	92%
$CaCl_2 \cdot 6H_2O$	29%	$SrCl_2 \cdot 6H_2O$	71%	K_2SO4	97%
KF	31%	$NaNO_3$	74%	K_2CrO_4	98%

Hydrated Salts

- **Two significant problems:**
  1. Stabilization is assumed to form oxides but experimental evidence suggests the hydrolysis is incomplete.
  2. Small amounts of these salts can absorb sufficient water at very low atmospheric moisture to fail the 0.5wt% moisture criterium – 22 g of $MgCl_2$ and 26 g of $CaCl_2$, out of 5000 g of material.

Thermal Decomposition of Magnesium Compounds A Key Uncertainty

Mechanism 1 (Petzold and Naumann 1980)

$MgCl_2{\cdot}6H_2O \rightarrow MgCl_2{\cdot}4H_2O + 2H_2O$ 117 °C

$MgCl_2{\cdot}4H_2O \rightarrow MgCl_2{\cdot}2H_2O + 2H_2O$ 190 °C

$2\ MgCl_2{\cdot}2H_2O \rightarrow MgCl_2{\cdot}Mg(OH)_2{\cdot}2H_2O + 2HCl$ 230 °C

$MgCl_2{\cdot}Mg(OH)_2{\cdot}2H_2O \rightarrow 2{\cdot}Mg(OH)Cl + 2H_2O$ 290 °C

Mechanism 2 (Kirsh, Yariv et al. 1987)

$MgCl_2{\cdot}xH_2O \rightarrow MgCl_2{\cdot}(x - y)H_2O + yH_2O$

$MgCl_2{\cdot}H_2O \rightarrow Mg(OH)Cl + HCl$ or

$2MgCl_2{\cdot}3H_2O \rightarrow Mg_2(OH)_3Cl + 3HCl$ etc.

$Mg(OH)Cl \rightarrow MgO + HCl$

$Mg(OH)_2(\text{amorphous}) + MgCl_2 \rightarrow 2\ MgO + 2\ HCl$ or

$2\ Mg(OH)Cl \rightarrow MgO{\cdot}MgCl_2 + H_2O$ etc.

Mechanism 4 (Galwey and Laverty 1989)

$MgCl_2{\cdot}2H_2O \rightarrow Mg(OH)Cl + H_2O + HCl$ {fast}

$Mg(OH)Cl \rightarrow MgO + HCl$ {slow}

Behavior of Hydrated Salts

The equilibrium vapor pressure of water over hydrated salts of magnesium chloride at two temperatures. The heat of adsorption was calculated from the heats of formation given in the literature. Danes, F. E.,Saint-Aman, E., and Coudurier, L., (1988) "Etude Thermodynamique de la Decomposition Thermique des Hydrates du Chlorure de Magnesium", Journal of Thermal Analysis 34, 821-833.

24 °					
Species	$\Delta H_{ads}(298)$	$\Delta\Phi^{o}$	$\Delta G^{o}/T$	P/Torr	RH (at 24 C)
water	0	118.8798	29.207	22.39220235	100.0%
$MgCl_2$ $6H_2O$	13.696	118.8798	75.298	0.08748319	0.39%
$MgCl_2$ $4H_2O$	22.696	118.8798	105.586	0.00229009	0.010%
$MgCl_2$ $2H_2O$	27.196	118.8798	120.730	0.00037053	0.0017%
$MgCl_2$ $1H_2O$	39.596	118.8798	162.460	0.00000245	0.000011%
100 °C					
water	0	118.8798	0.005	761	3398.6%
$MgCl_2$ $6H_2O$	13.696	118.8798	36.709	9.07	40.5%
$MgCl_2$ $4H_2O$	22.696	118.8798	60.828	0.499	2.23%
$MgCl_2$ $2H_2O$	27.196	118.8798	72.888	0.117	0.522%
$MgCl_2$ $1H_2O$	39.596	118.8798	106.118	0.00215	0.0096%

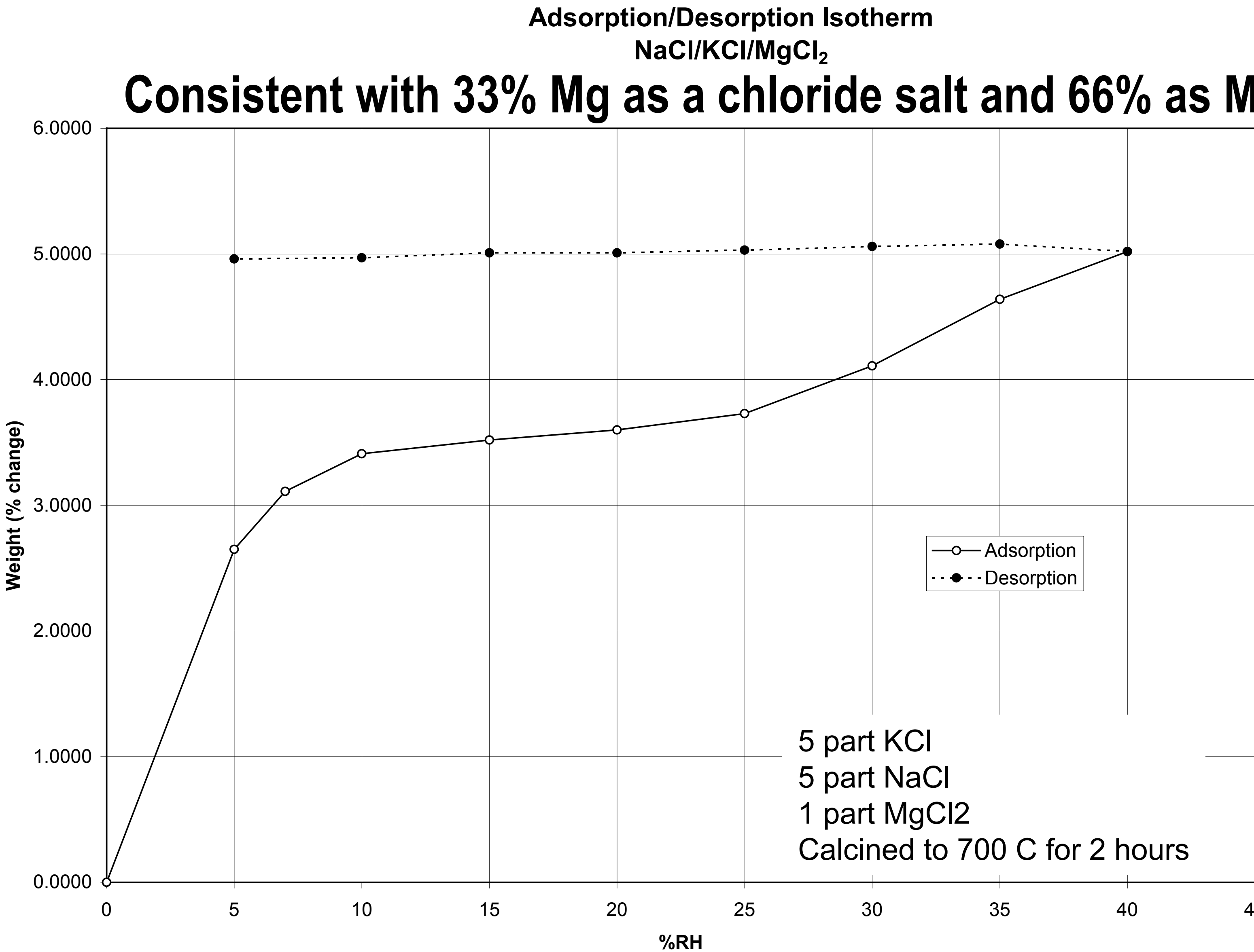
Preparation of NaCl, KCl, $MgCl_2$ sample

Constituent	Mass [mg]
KCl	464.9
NaCl	465.1
$MgCl_2 \cdot 6H_2O$	208.8
Total	1138.8

Constituent	MW	mmoles	Mole fraction	Mass (w/o H_2O)	Mass (hydrolysed)
KCl	74.551	6.24	0.29	464.9	464.9
NaCl	58.443	7.96	0.37	465.1	465.1
$MgCl_2$	95.210	1.03	0.05	98.1	-
H_2O	18.015	6.16	0.29	-	-
MgO	40.304	-	-	-	41.5
Total		21.39		1028.1	971.5

- Weighed individual chemicals out.
- Mixed in boat.
- Calcined to 700 ºC. Inserted into oven at 9:58 am. Reached 700 ºC at 10:20 am. Removed from furnace at 12:20 after two hours at temperature.
- Total weight after calcination – 986.9 mg.
- Ground in mortal and pestle and placed into sample vial.

Consistent with 33% Mg as a chloride salt and 66% as MgO.



Calcination weight and Moisture Reabsorption Consitent with 66% hydrolyzed $MgCl_2$

Constituent	MW	mmoles	Mole fraction	Mass (w/o H_2O)	Mass (hydrolyzed)	Mass (67% hydrolyzed)
KCl	74.551	6.24	0.29	464.9	464.9	464.9
NaCl	58.443	7.96	0.37	465.1	465.1	465.1
$MgCl_2$	95.210	1.03	0.05	98.1	-	32
H_2O	18.015	6.16	0.29	-	-	(37)
MgO	40.304	-	-	-	41.5	27
Total		21.39		1028.1	971.5	989

Binary salts should form in common compositions used for processing

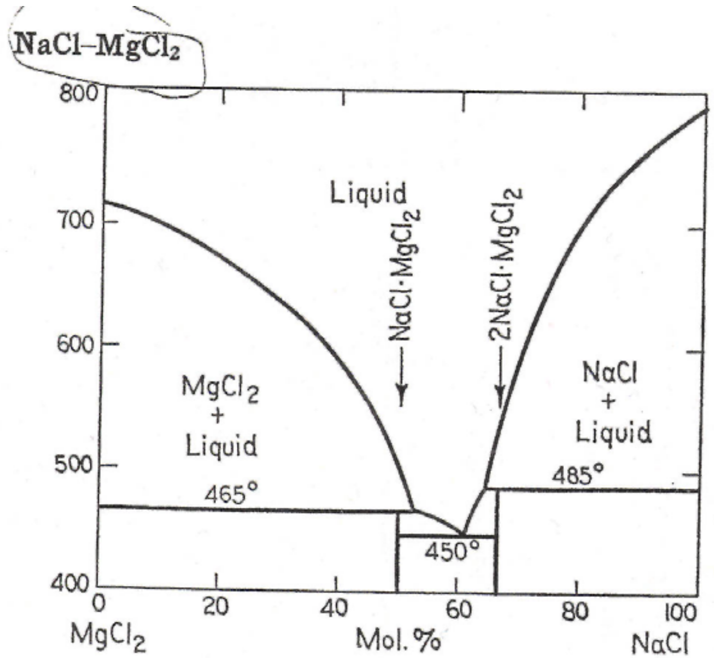


FIG. 1307.—System NaCl–MgCl$_2$.

W. Klemm and P. Weiss, *Z. anorg. u. allgem. Chem.*, **245**, 281 (1940).

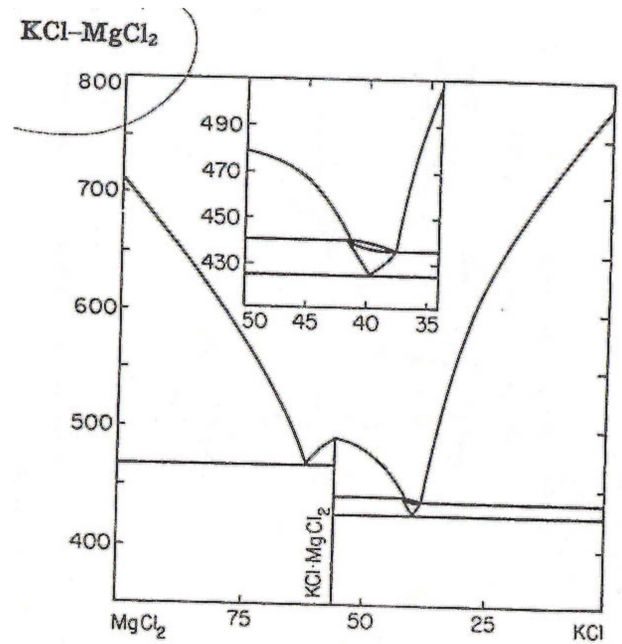
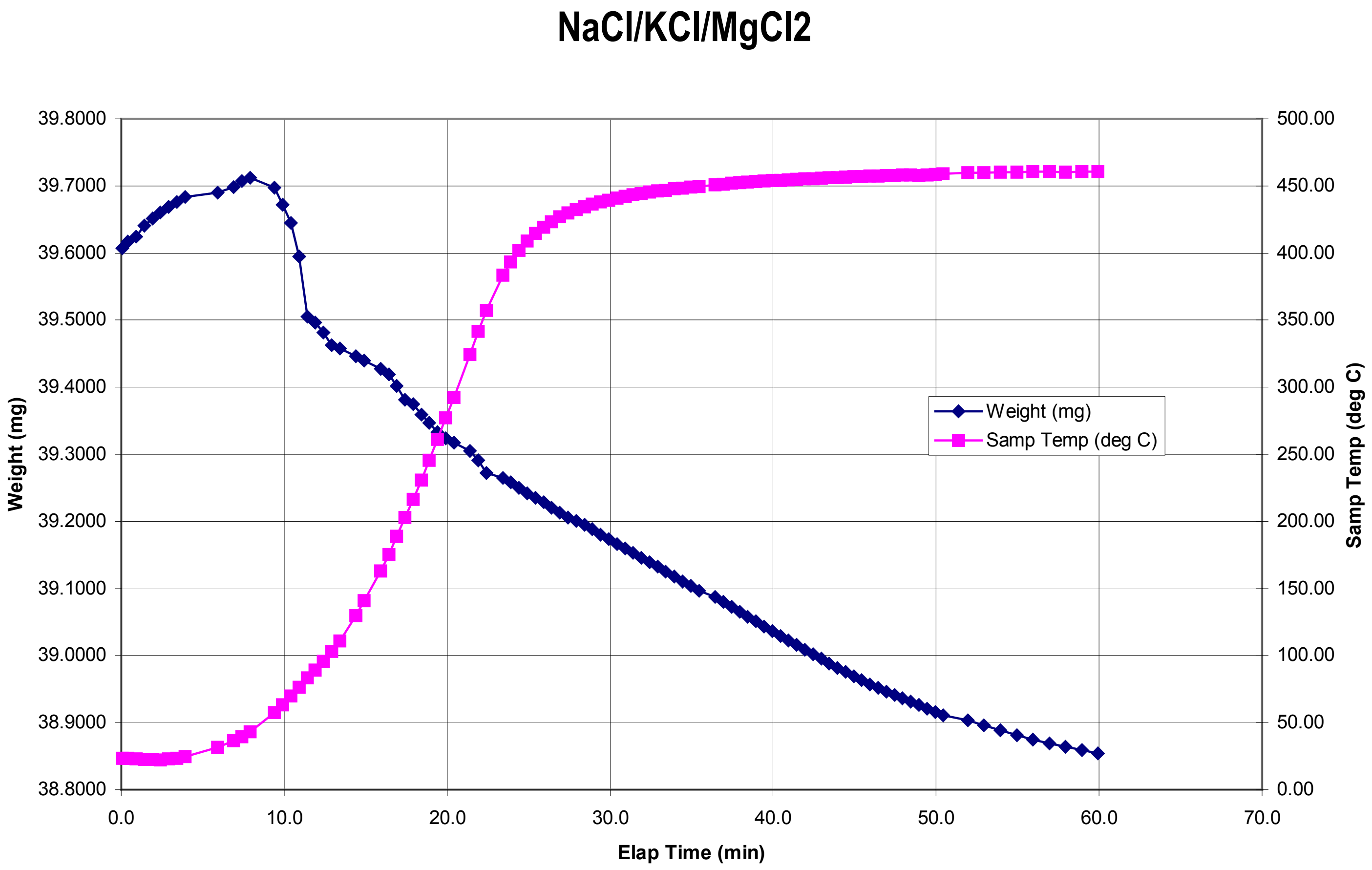


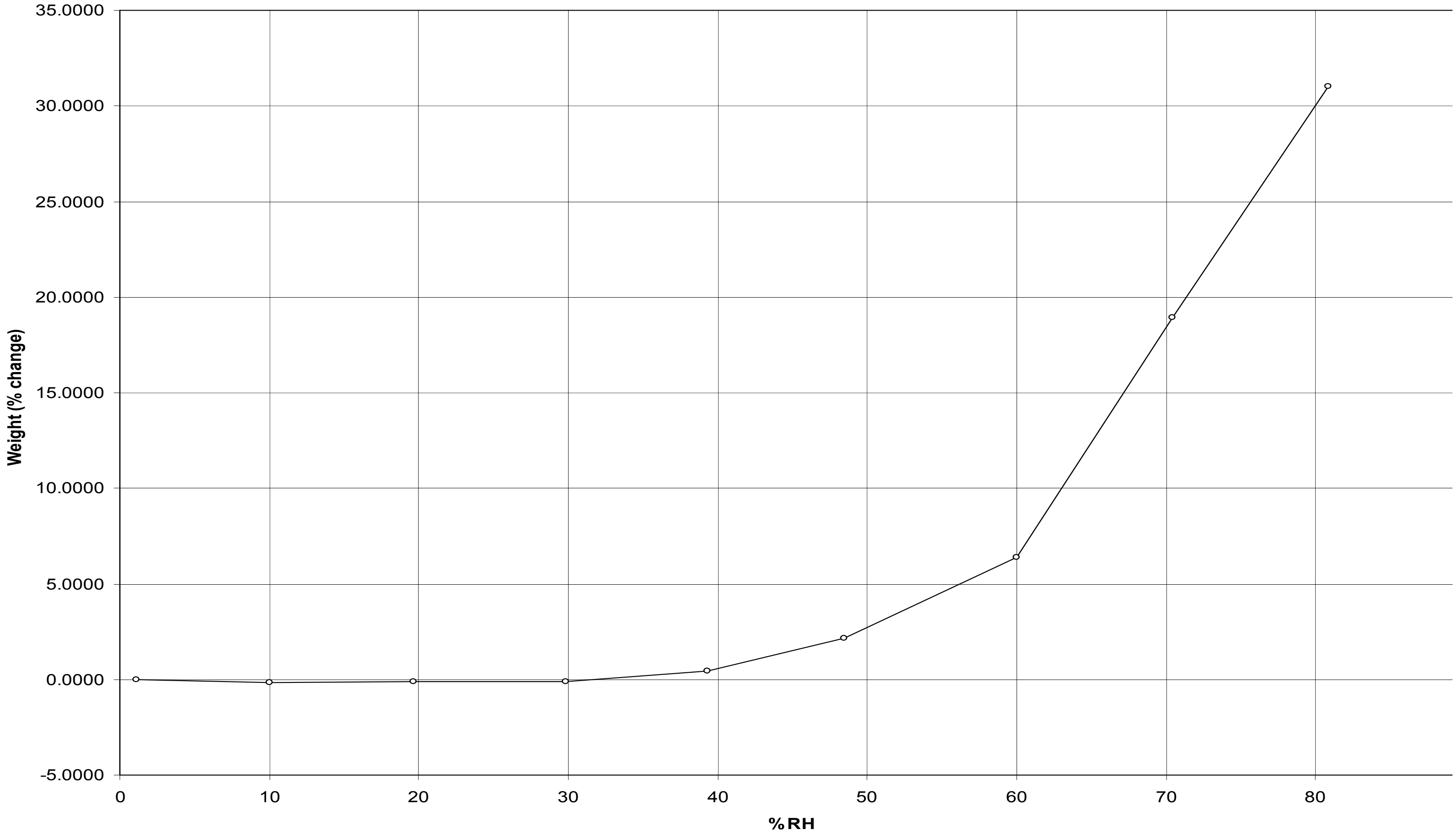
FIG. 1267.—System KCl–MgCl$_2$.

A. I. Ivanov, *Sbornik Stateĭ Obshcheĭ Khim., Akad. Nauk S.S.S.R.*, 1, 758 (1953).

Drying Sample Shows Loss of Water and Evaporation of Salt



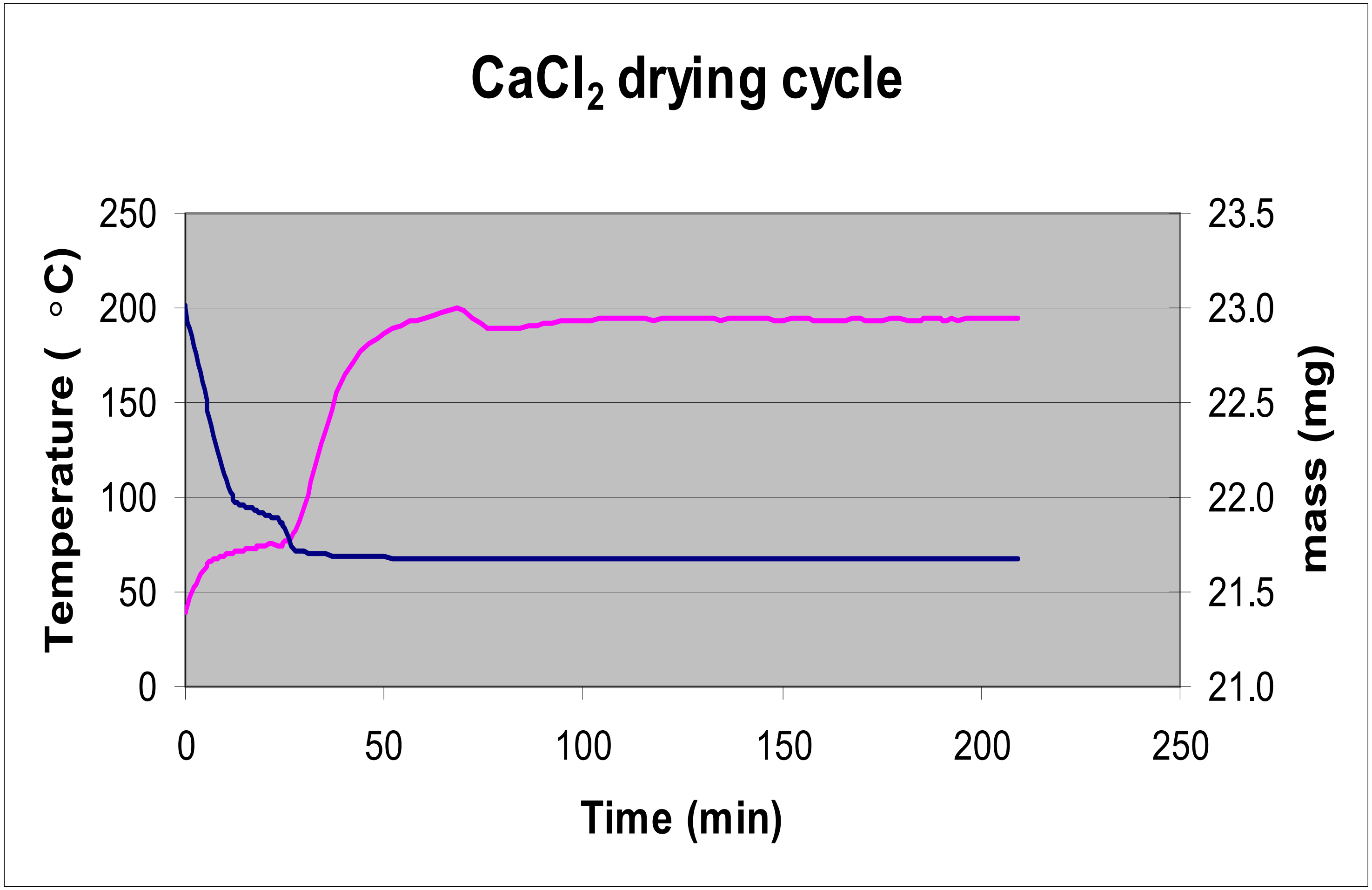
KCl/NaCl/$MgCl_2$ Adsorption isotherm



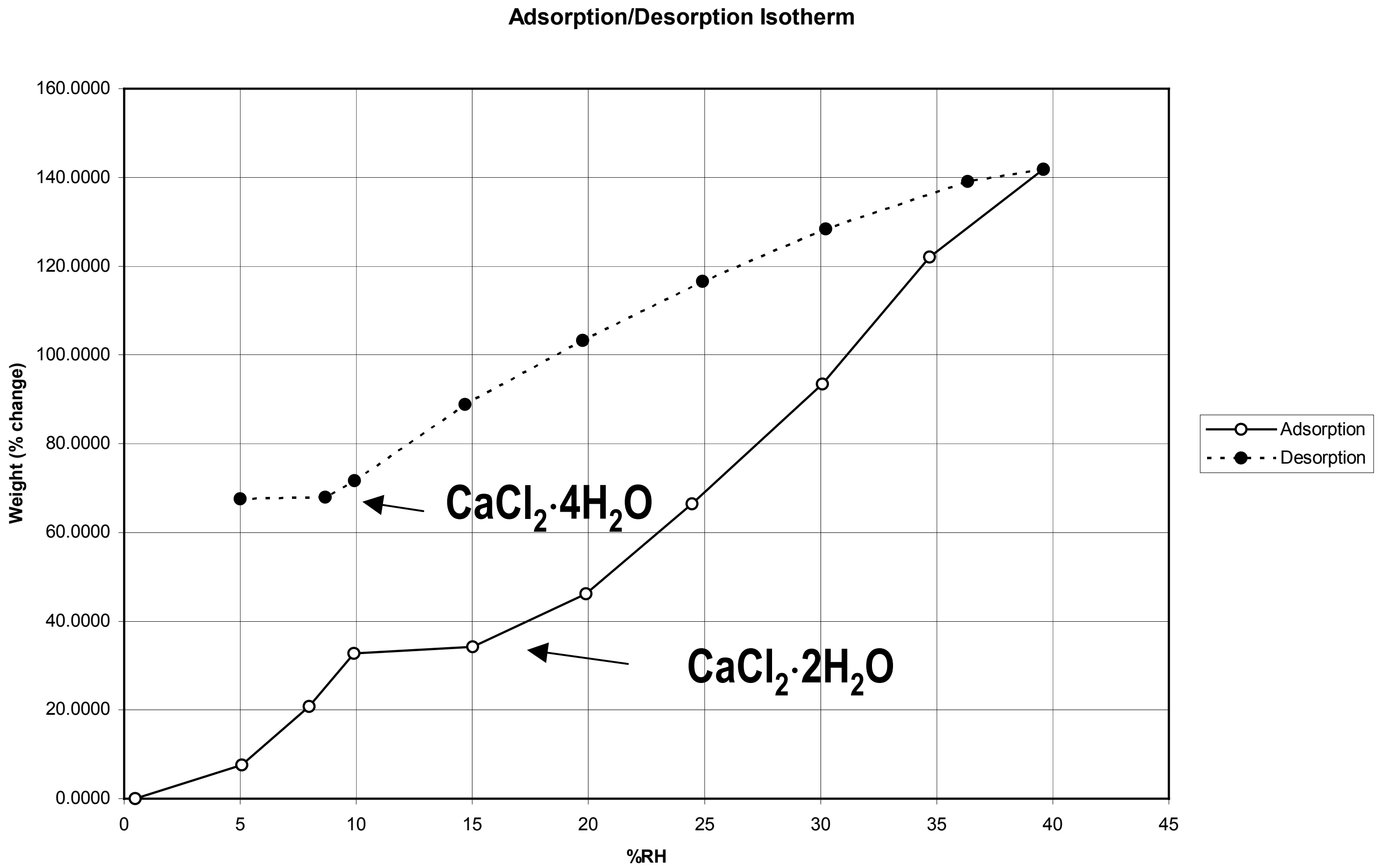
Moisture Sorption of $CaCl_2$

- Dried at 700 °C for 2 hours, ground.
- Dried in apparatus at 200 °C.
- Pure material forms the anhydrous salt.
- Moisture sorption forms a series of hydrated salts

CaCl2 Losses All Waters of Hydration by 100 °C

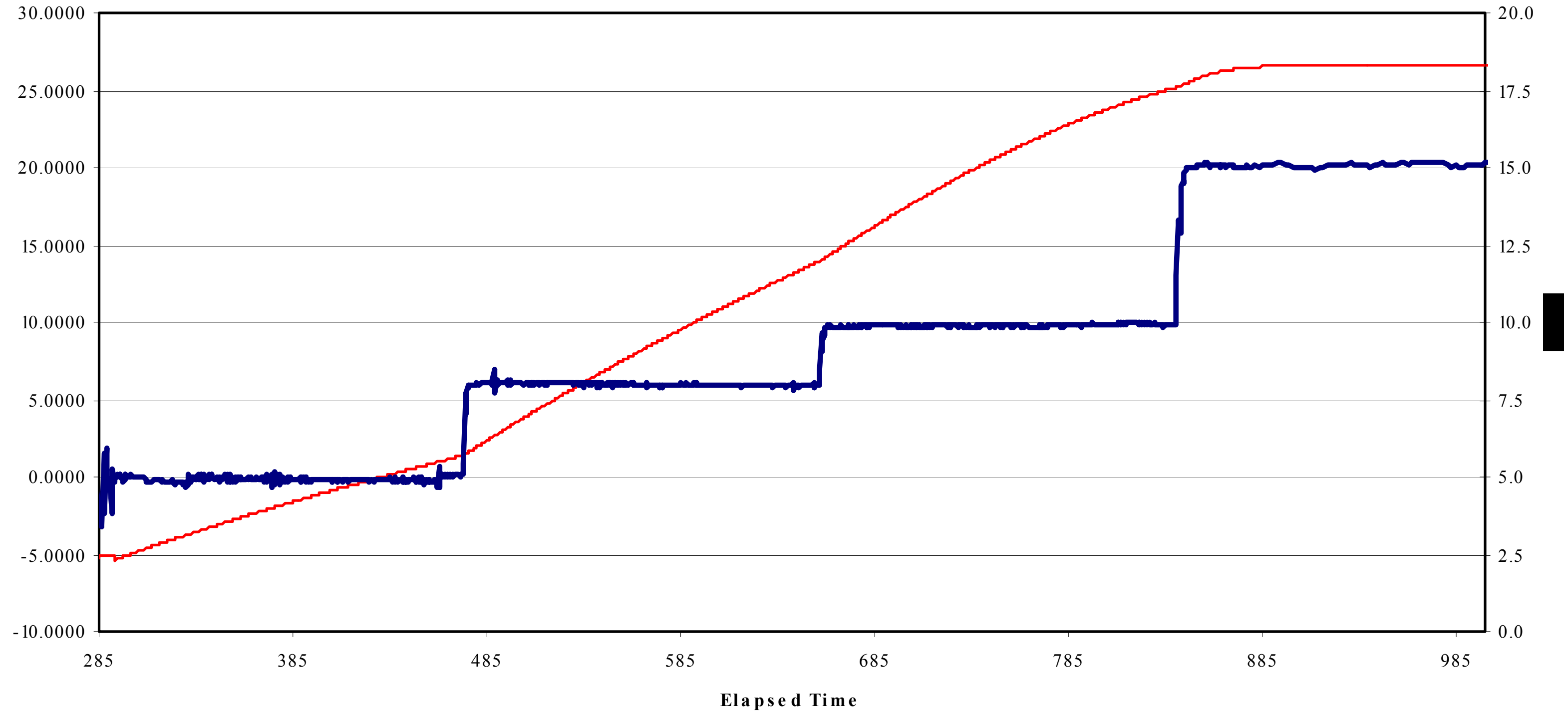


$CaCl_2$ Moisture Adsorption Behavior Shows Formation of Specific Hydrates

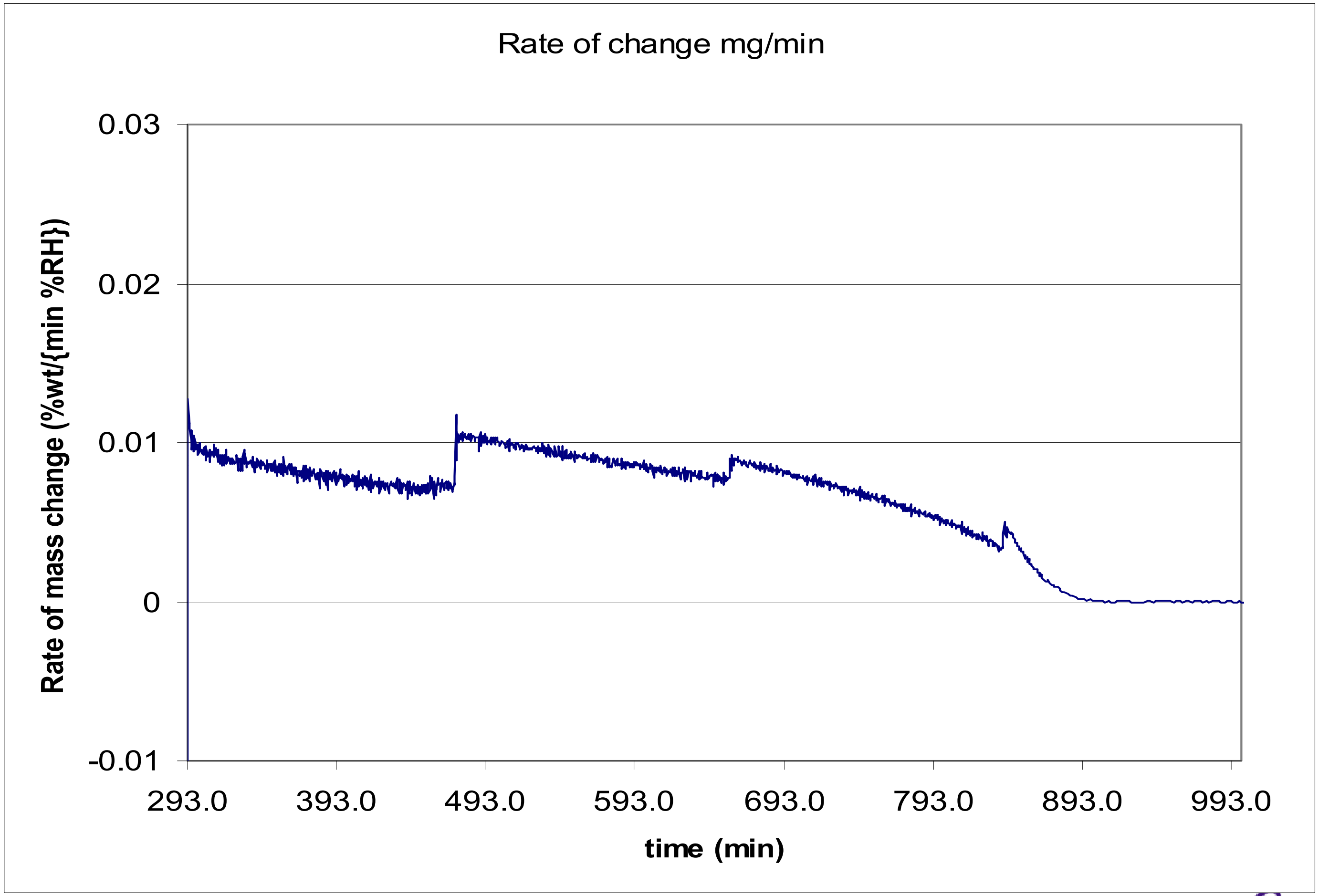


Moisture Sorption Not at Equilibrium at Low RH

Time Course for $CaCl_2$



Rate of mass change normalized to the relative humidity



Rate of moisture uptake for salt and salt mixtures

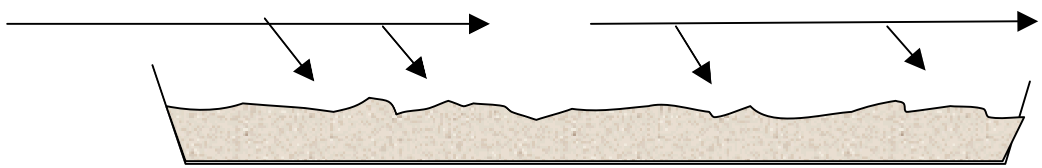
- $CaCl_2$ at low RH maximum rate of moisture uptake is 0.01 wt%/min for each %RH.
- $NaCl/KCl/MgCl_2$ mixture heated in apparatus to 450 C at high RH is 0.002 wt%/min for each %RH.

Future Work

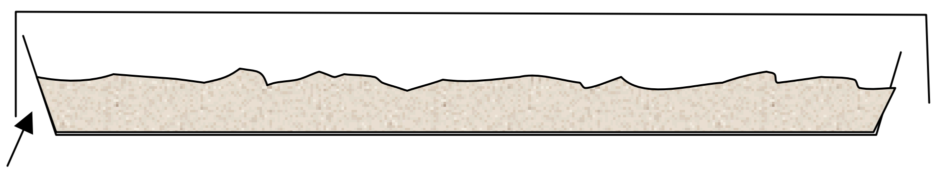
- More Investigations on Binary Salts
- Effect of Calcination on Formation of Hydrophobic Surfaces That Inhibit Moisture Sorption
- Introduction of Apparatus into Glove Box to Study MIS Materials
- Study the amount of water adsorbed onto plutonium oxide prior to physical sorption.

Kinetics

Glove box air replacement constantly renews atmospheric moisture above uncovered calcination boat.



Covering calcination boat immediately following stabilization will significantly reduce moisture reabsorption prior to packaging.



Water diffusion
through small
openings

Conclusions

•Metal oxides (except some alkali metal oxides) will not absorb moisture up to 60% RH.

•Deliquescent salts will not absorb moisture at the 1000 ppm_v and 300 ppm_v moisture levels proposed for RFETS and Hanford.

•Hydrated salts may absorb enough water to fail the 0.5wt% moisture criterium. This potential can be avoided by covering the calcination boat immediately following stabilization up to the time of packaging.